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JC809 U.S. PTO

**UTILITY
PATENT APPLICATION
TRANSMITTAL**

Only for new nonprovisional applications under 37 CFR 1.53(b)

Attorney Docket No.

AD6731 US NA

First Named Inventor or Application Identifier

Robert Joseph Statz

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April 27, 2000

JC809 U.S. PTO

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APPLICATION ELEMENTS

See MPEP chapter 600 concerning utility patent application contents.

ADDRESS TO:

Assistant Commissioner for Patents
Box Patent Application
Washington, DC 20231

1. ☒ Fee (Authority to charge deposit account below.)
(Submit an original, and a duplicate for fee processing)
2. ☒ Specification [Total Pages (preferred arrangement set forth below)
- Descriptive title of the invention
 - Cross References to Related Applications (if needed)
 - Statement Regarding Fed sponsored R & D (if needed)
 - Reference to Microfiche Appendix (if filed)
 - Background of the Invention
 - Brief Summary of the Invention
 - Brief Description of the Drawings (if filed)
 - Detailed Description
 - Claim(s)
 - Abstract of the Disclosure
3. ☐ Drawing(s) (35 USC 113) [Total Sheets

4. ☒ Oath or Declaration [Total Pages
 - a. ☒ Newly executed (original or copy)
 - b. ☐ Copy from a prior application (37 CFR 1.63(d))
(for continuation/divisional with Box 14 completed)
 - i. ☐ **DELETION OF INVENTORS**
Signed Statement below at 15 deleting
inventor(s) named in the prior application,
see 37 CFR 1.63(d)(2) and 1.33(b).

5. ☐ Incorporation by Reference (useable if Box 4b is checked)
The entire disclosure of the prior application, from which a
copy of the oath or declaration is supplied under Box 4b, is
considered as being part of the disclosure of the
accompanying application and is hereby incorporated by
reference therein.

6. ☐ Microfiche Computer Program (Appendix)
7. Nucleotide and/or Amino Acid Sequence Submission
(if applicable, all necessary)
- a. ☐ Computer Readable Copy
 - b. ☐ Paper Copy (identical to computer copy)
 - c. ☐ Statement verifying identity of above copies

ACCOMPANYING APPLICATION PARTS

8. ☐ Power of Attorney
9. ☐ Information Disclosure
Statement (IDS)/Cover Letter plus PTO-1449 ☐ Copies of IDS
Citations
10. ☐ Preliminary Amendment
11. ☒ Return Receipt Postcard (MPEP 503)
(Should be specifically itemized)
12. ☐ Certified Copy of Priority Document(s)
(if foreign priority is claimed)
13. ☐ Other:

14. If a CONTINUING APPLICATION, check appropriate box and supply the requisite information:

☐ Continuation ☐ Divisional ☒ Continuation-in-part (CIP) of prior Application No.: 09/422,142

15. ☐ **DELETION OF INVENTOR(S) STATEMENT:** This application is being filed by less than all the inventors named in the prior application. In accordance with 37 CFR 1.63(d)(2) and 1.33(b), the Assistant Commissioner is requested to delete the name(s) of the following person or persons who are not inventors of the invention being claimed in this application:
16. ☐ Amend the specification by inserting before the first line the sentence:
-- This is a ☐ continuation-in-part, ☐ continuation, ☐ division of Application No. _____ filed
, now abandoned. --
17. ☐ Cancel in this application original claims ____ of the prior application before calculating the filing. (At least one
original independent claim must be retained for filing purposes.)
18. ☐ Priority of foreign Application No. _____ filed on _____ in
_____ is claimed under 35 U.S.C. 119.
(country)

CLAIMS	(1) FOR	(2) NUMBER FILED	(3) NUMBER EXTRA	(4) RATE	(5) CALCULATIONS
	TOTAL CLAIMS (37 CFR 1.16(c))	9 - 20 =	0	x \$ 18 =	0
	INDEPENDENT CLAIMS (37 CFR 1.16(b))	2 - 3 =	0	x \$ 78 =	0
	MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$ 260 =	0
				BASIC FEE (37 CFR 1.16(a))	+ \$ 690.00
				TOTAL =	\$ 690.00

19. The Commissioner is hereby authorized to credit overpayments or charge the following fees to Deposit Account No. 04-1928:

a. ☒ Fees required under 37 CFR 1.16.

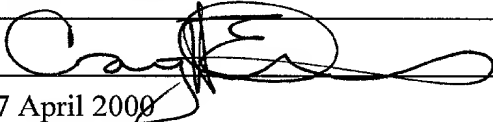
b. ☒ Fees required under 37 CFR 1.17.

20. ☐ Other:

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22. SIGNATURE OF ATTORNEY OR AGENT REQUIRED

NAME	Craig H. Evans	REG. NO.: 31,825
SIGNATURE		
DATE	27 April 2000	

TITLE

HIGHLY-NEUTRALIZED ETHYLENE COPOLYMERS

BACKGROUND OF THE INVENTION

This application claims priority to co-pending U.S. Patent
5 Application Serial No. 09/422,142, which is incorporated herein by
reference.

Field of the Invention

The invention relates to melt-processable, highly-neutralized
ethylene, C_3 to C_8 α,β ethylenically unsaturated carboxylic acid
10 copolymers and process for making them. It relates to such copolymers,
neutralized to greater than 90%, particularly to those neutralized to nearly
to or to 100%. These copolymers are made by incorporating a sufficient
amount of specific organic acid (or salt) into the copolymer before
neutralization to the high level. These copolymers are useful in making
15 molded products such as golf ball components, thermoplastic shoe soles
for cleated footwear, and resilient foams for sporting goods.

Description of Related Art

Ionomers of acid copolymers of alpha olefins, particularly
ethylene, and C_{3-8} α,β ethylenically unsaturated carboxylic acid, have been
20 known for a long time. U.S. Patent No. 3,264,272 (Rees) teaches
methods for making such ionomers from "direct" acid copolymers. "Direct"
copolymers are polymers polymerized by adding all monomers
simultaneously, as distinct from a graft copolymer, where another
monomer is grafted onto an existing polymer, often by a subsequent free
25 radical reaction. A process for preparing the acid copolymers on which
the ionomers are based is described in U.S. Patent No. 4,3451,931.

The acid copolymers may contain a third softening monomer
such as an alkyl acrylate or methacrylate. The ethylene acid copolymers
can be described as an E/X/Y copolymers where E is ethylene, X is the
30 α,β ethylenically unsaturated carboxylic acid, particularly acylic and
methacrylic acid, and Y is a softening comonomer such as a C_1 TO C_8

alkyl acrylate or methacrylate ester. X and Y can be present in a wide range of percentages, X typically up to about 35 weight percent (wt.%) of the polymer and Y typically up to about 50 weight percent of the polymer.

The wide range of neutralization of the acid moiety in the acid copolymer by a wide range of cations is known. Typical cations include lithium, sodium, potassium, magnesium, calcium, barium, lead, tin, zinc, aluminum, and combinations of such cations. Neutralization to 90% and higher, including up to 100%, is known, but there remains a need to achieve such a high degree of neutralization without loss of melt-processability or properties such as elongation and toughness. This is particularly so for copolymers with high acid levels and when using cations other than barium, lead and tin to neutralize the copolymer.

SUMMARY OF THE INVENTION

It has been found that, by modifying an acid copolymer or ionomer with a sufficient amount of specific organic acids (or salts thereof); it is possible to highly neutralize the acid copolymer without losing processability or properties such as elongation and toughness. The organic acids employed in the present invention are aliphatic, mono-functional, saturated or unsaturated organic acids, particularly those having fewer than 36 carbon atoms.

The thermoplastic composition of this invention consists essentially of (a) aliphatic, mono-functional organic acid(s) having fewer than 36 carbon atoms; and (b) ethylene, C_3 to C_8 α,β ethylenically unsaturated carboxylic acid copolymer(s) and ionomer(s) thereof, wherein greater than 90%, preferably near 100%, and more preferably 100% of all the acid of (a) and (b) are neutralized.

With the addition of sufficient organic acid, greater than 90%, nearly 100%, and preferably 100% of the acid moieties in the acid copolymer from which the ionomer is made can be neutralized without losing the processability and properties of elongation and toughness.

The melt-processable, highly-neutralized acid copolymer ionomer can be produced by

(a) melt-blending ethylene α,β ethylenically unsaturated C_{3-8} carboxylic acid copolymer(s) or ionomer(s) thereof that are not neutralized to the level that they have become intractable (not melt-processable) with one or more aliphatic, mono-functional, saturated or unsaturated organic acids having fewer than 36 carbon atoms or salts of the organic acids, and then

(b) Adding a sufficient amount of a cation source to increase the level of neutralization all the acid moieties (including those in the acid copolymer and in the organic acid) to greater than 90%, preferably near 100%, more preferably to 100%.

DETAILED DESCRIPTION OF THE INVENTION

In this disclosure, the term "copolymer" is used to refer to polymers containing two or more monomers. The phrase "copolymer of various monomers" means a copolymer whose units are derived from the various monomers. "Consisting essentially of" means that the recited components are essential, while smaller amounts of other components may be present to the extent that they do not detract from the operability of the present invention. The term "(meth) acrylic acid" means methacrylic acid and/or acrylic acid. Likewise, the term "(meth) acrylate" means methacrylate and/or acrylate.

All references set forth herein are incorporated by reference.

Acid Copolymers

The acid copolymers used in the present invention to make the ionomers are preferably 'direct' acid copolymers. They are preferably alpha olefin, particularly ethylene, C_{3-8} α,β ethylenically unsaturated carboxylic acid, particularly acrylic and methacrylic acid, copolymers. They may optionally contain a third softening monomer. By "softening", it is meant that the polymer is made less crystalline. Suitable "softening" comonomers are monomers selected from alkyl acrylate, and alkyl methacrylate, wherein the alkyl groups have from 1 - 8 carbon atoms.

Organic acids and Salts

The organic acids employed in the present invention are aliphatic, mono-functional (saturated, unsaturated, or multi-unsaturated) organic acids, particularly those having fewer than 36 carbon atoms. Also salts of these organic acids may be employed. The salts may be any of a wide variety, particularly including the barium, lithium, sodium, zinc, bismuth, potassium, strontium, magnesium or calcium salts of the organic acids.

While it may be useful for the organic acids (and salts) to have a low volatility when being melt-blended with acid copolymer or ionomer, volatility has been found to not be limiting when neutralizing the blend to high levels, particularly near to or at 100%. At 100% neutralization (all acid in copolymer and organic acid neutralized), volatility simply is no longer an issue. As such, organic acids with lower carbon content can be used. Particularly useful organic acids include C_4 to less than C_{36} (say C_{34}), C_6 to C_{26} , particularly C_6 to C_{18} , particularly C_6 to C_{12} , organic acids. Particular organic acids useful in the present invention include caproic acid, caprylic acid, capric acid, lauric acid, stearic acid, behenic acid, erucic acid, oleic acid, and linoelic acid.

Process for making Highly-Neutralized Ionomer

The melt-processable, highly-neutralized acid copolymer ionomer of the present invention can be produced by

(a) melt-blending ethylene α,β ethylenically unsaturated C_{3-8} carboxylic acid copolymer(s) or ionomer(s) thereof that are not neutralized to the level that they have become intractable (not melt-processable) with one or more aliphatic, mono-functional, saturated or unsaturated organic acids having less than 36 carbon atoms or salts of the organic acids, and concurrently or subsequently

(b) Adding a sufficient amount of a cation source to increase the level of neutralization all the acid moieties (including those in

the acid copolymer and in the organic acid) to greater than 90%, preferably near 100%, more preferably to 100%.

Neutralization of acid copolymers and organic acids in this manner (concurrently or subsequently) has been found to be the only way without the use of an inert diluent to neutralize the copolymer without loss of processability or properties such as toughness and elongation to a level higher than that which would result in loss of melt processability and properties for the ionomer alone. For example, an acid copolymer can be neutralized to over 90%, preferably to about 100% or to 100% neutralization without losing the melt processability associated with acid copolymers neutralized to greater than 90%. In addition, neutralizing to about 100% or to 100% reduces the deposits of the organic acids on the mold vent observed upon molding mixtures with less than 100% neutralization.

The acid copolymer(s) or unmodified ionomer(s) can be melt-blended with the organic acid(s) or salt(s) in any manner known in the art. For example, a salt and pepper blend of the components can be made and the components can then be melt-blended in an extruder.

The still melt-processable, acid-copolymer/organic-acid-or-salt blend can be neutralized or further neutralized by methods known in the art. For example, a Werner & Pfleiderer twin screw extruder can be used to neutralize the acid copolymer and the organic acid at the same time.

Depending on the acid level of the co- or ter-polymer, the level of organic acid that controls processability can be determined based on the disclosures herein. The percent organic acid needs to be higher for higher acid levels in the backbone of co- or terpolymer. See, for example the following table comparing melt indices obtained for various acid levels in an E/14-16%*n*BA/AA terpolymer. Less of a lower molecular weight organic acid is needed to have the same effect as a higher amount of a higher molecular weight organic acid.

Table 1
Comparing M.I. To Stearic Acid Level and %AA

Acid Level	M.I. Base Resin	Stearic Acid Level				
		20%	30%	35%	40%	45%
8.1%AA	67.9			1.8	2	6
About 8.3%AA	62.5			1.08	1.13	2.25
10.1%AA	66.8			0.62	1.55	2.22
About 6.8%AA	75	1.25	1.92		6.52	
About 4.9%AA	86	4.9	9.7		23.2	

Highly-Neutralized, Melt-Processable Ionomer

5 The resulting thermoplastic composition of this invention consists essentially of (a) aliphatic, mono-functional organic acid(s) having fewer than 36 carbon atoms; and (b) ethylene, C₃ to C₈ α,β ethylenically unsaturated carboxylic acid copolymer(s) and ionomer(s) thereof, wherein greater than 90%, preferably near 100%, and more preferably 100% of all
10 the acid of (a) and (b) are neutralized.

 This resulting highly neutralized; melt-processable acid copolymer of this invention can be melt-blended with other components to produce end products. For example, it may be melt-blended with components employed in co-pending U.S. Application Serial No.
15 09/422,142 to make one-, two-, three-piece, and multi-layered golf balls and foamed materials useful in footwear and other sport balls such as softballs. The components used with the resulting highly neutralized, melt-processable acid copolymer in this case include thermoplastic polymer components selected from copolyetheresters,
20 copolyetheramides, elastomeric polyolefins, styrene diene block copolymers and thermoplastic polyurethanes; and fillers.

Testing Criteria for Examples

 Coefficient of Restitution (COR) is measured by firing an injection-molded neat sphere of the resin having the size of a golf ball
25 from an air cannon at a velocity determined by the air pressure. The initial velocity generally employed is 125 feet/second. The ball strikes a steel plate positioned three feet away from the point where initial velocity is

determined, and rebounds through a speed-monitoring device. The return velocity divided by the initial velocity is the COR.

PGA Compression is defined as the resistance to deformation of a golf ball, measured using an Atti machine.

5 Tensile properties (tensile at break, elongation at break, tensile yield, and elongation yield) are determined in accord with ASTM D1708.

Examples

10 Numbers in parentheses in the tables represent the weight percentage of the component in the blend.

Employing a Werner & Pfleiderer twin screw extruder, 4812 grams of stearic acid were added to 7218 grams of an E/23nBA/9.6MAA polymer. Enough magnesium hydroxide was added to this mixture to neutralize 90 % and more than 95% of the available acid. (See Ex 1a & 1b
15 in Table 1).

Two other resins with the composition cited in Table 2 were reacted with stearic acid and magnesium hydroxide. However, in this case, enough magnesium hydroxide was added to neutralize 100% of the available combined acids. These mixed anionic ionomers Ex 1c and 1d
20 are listed in Table 2.

Table 2
Magnesium Stearate Modified Magnesium Ionomers

Ex No	Resin Comp.	Cation Type	Organic Acid (%)	% Neut	M.I. (g/10min)
1a	E/23nBA/9.6MAA	Mg	Stearic(40)	90	5.2
1b	E/23nBA/9.6MAA	Mg	Stearic(40)	95	3.6
1c	E/15nBA/8.5AA	Mg	Stearic(40)	>100	1.15
1d	E/16nBA/12AA	Mg	Stearic(40)	>100	0.09

25 Properties of the 100% neutralized resin of Example 1c are set forth in the following Table 3.

Table 3

PGA Comp	COR	Tensile at Break (psi)	Tensile Yield (psi)	Elongation at Break (%)	Elongation Yield (%)
90	.787	2802	2069	340	28

202407460650

CLAIMS

1. A thermoplastic composition that is melt-processable consisting essentially of (a) aliphatic, mono-functional organic acid(s) having fewer than 36 carbon atoms; and (b) ethylene, C₃ to C₈ α,β ethylenically unsaturated carboxylic acid copolymer(s) and ionomer(s) thereof, wherein greater than 90% of all the acid of (a) and (b) is neutralized.
2. The composition of claim 1 wherein about 100% of the acid in (a) and (b) is neutralized.
3. The composition of claim 1 wherein an amount of cation source in excess of the amount required to neutralize 100% of the acid in (a) and (b) is used to neutralize the acid in (a) and (b).
4. The composition of claim 1 wherein the organic acid is one or more C₆ to C₂₆ organic acids.
5. The composition of claim 4 wherein the organic acid is one or more C₆ to C₁₈ organic acids.
6. The composition of claim 5 wherein the organic acid is one or more of C₆ to C₁₂ organic acids,
7. A process to make a highly-neutralized, melt-processable ionomer comprising the steps of
 - (a) Melt-blending an ethylene α,β ethylenically unsaturated carboxylic acid copolymer or a melt-processable ionomer thereof with an organic acid or a salt of organic acid, and
 - (b) concurrently or subsequently adding sufficient cation source to neutralize more than 90% of all the acid moieties of the acid copolymer or ionomer thereof and the organic acid or salt thereof.
8. The process of claim 7 wherein about 100% of the acid moieties are neutralized.
9. The process of claim 7 wherein the amount of cation source is in excess of the amount that is required to neutralize all the acid moieties in the acid copolymer or ionomer thereof and the organic acid or salt thereof.

TITLE

HIGHLY-NEUTRALIZED ETHYLENE COPOLYMERS

ABSTRACT OF THE DISCLOSURE

5 Melt-processable, highly-neutralized ethylene, C_3 to C_8 α,β
ethylenically unsaturated carboxylic acid copolymers and process for
making them. Copolymers are made by incorporating a C_4 to less than a
 C_{36} aliphatic, mono-functional organic acid and neutralizing greater than
90% to 100% of the acid groups present concurrently with or subsequently
10 to the incorporation of the organic acid.

DECLARATION and POWER OF ATTORNEY

As a below-named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Highly-Neutralized Ethylene Copolymers

the specification of which is attached hereto unless the following box is checked:

☐ was filed on _____ as U.S. Application No. _____ or PCT International Application No. _____ and was amended on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is known to me to be material to patentability as defined in 37 CFR § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Application No.	Country	Filing Date	Priority Claimed (Yes/No)
-----------------	---------	-------------	---------------------------

I hereby claim the benefit under 35 U.S.C. § 119(e) of any United States Provisional Application(s) listed below.

U.S. Provisional Application No.	U.S. Filing Date
----------------------------------	------------------

I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International Application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application or PCT International Application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is known to me to be material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

Application No.	Filing Date	Status (patented, pending or abandoned)
09/422,142	10/21/99	Pending

POWER OF ATTORNEY: I hereby appoint the following attorney(s) and/or agent(s) the power to prosecute this application and transact all business in the Patent and Trademark Office connected therewith:

Name: CRAIG H. EVANS	Registration No. 31,825
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

INVENTOR(S)

Full Name of Inventor	Last Name STATZ	First Name ROBERT	Middle Name JOSEPH
	Signature (please sign full name): <i>Robert Joseph Statz</i>		Date: <i>April 27, 2000</i>
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☐ Additional Inventors are being named on separately numbered sheets attached hereto.